



Rigid linked dinuclear salph-co(III) catalyst for carbondioxide/epoxides copolymerization

Xiang Li^a, Ranlong Duan^a, Xuan Pang^{a,*}, Bo Gao^{a,b}, Xianhong Wang^a, Xuesi Chen^a

^a Key Laboratory of Polymer Ecomaterials, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

^b School of Materials Science and Engineering, Changchun University of Science and Technology, Changchun 130022, China

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ABSTRACT

Mononuclear and dinuclear salen-co(III) catalysts were designed for carbon dioxide (CO₂) and propylene oxide (PO) copolymerization. The dinuclear system maintained its activity with a turn over frequency (TOF) of 406 h⁻¹ at [PO]/[Cat] = 20,000. In contrast, the mononuclear catalyst system almost lost its activity with a TOF of 3 h⁻¹. The two cobalt centers in dinuclear structure may work synergistically due to the conjugated structure. This may contribute to the enhancement of the activity. The dinuclear catalyst system offered the highest molecular weight (Mn = 200,000) among reported dinuclear catalysts heretofore. Polymerization mechanism for the dinuclear catalyst system was postulated based on the subtly designed experiments. Synergy effect with the positive help of cocatalyst was explored. To further enhanced the thermal property of poly(propylene carbonate) (PPC), poly(cyclohexene carbonate) (PCHC) was incorporated. The glass transformation temperature of the copolymer of PPC-PCHC could be adjusted by the feed ratio of PO and cyclohexene oxide (CHO).

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1. Introduction

Carbon dioxide (CO₂) is a main origin of the unpopular greenhouse effect. Because it is inexpensive, abundantly available in high purity, and nonhazardous, CO₂ is considered as an ideal synthetic feedstock [1–4]. The innovative concept for beneficial use of CO₂ including the alternative coupling of CO₂ and epoxides to make degradable polycarbonates were popular. The first successful copolymerization of CO₂ and epoxide was reported by Inoue et al. in 1969 [5,6]. Inspired by Inoue's pioneering work, researchers have developed many catalysts [7–22]. Among them, salen-Co catalyst is one of the successful candidates [7,23–30]. To improve the performance of salen-Co catalysts, structures with piperidinium end-capping arms, quaternary ammonium salts or other functional groups were explored [31–35].

Recently, dinuclear catalysts have aroused much attention [36,37]. The two metal centers could work cooperatively in propylene oxide (PO) and CO₂ copolymerization. Nakano et al. prepared a series of flexibly linked dinuclear salen-co catalysts [38]. With a suitable distance, the two metal centers showed an obvious synergy

in high dilution, but the distance between the two metal centers resulted in a low selectivity of carbonate linkages. They proposed a bimetallic mechanism for the dinuclear catalyst in absence of cocatalyst. Klaus et al. designed flexibly linked dinuclear salen-cr complexes, the same trend upon dilution was observed as reported by Nozaki et al. [39]. The optimal dinuclear catalyst with a spacer length of *n* = 6 showed a TOF of 49 h⁻¹ at a [PO]/[Cr] ratio of 2000, and the TOF increased to 82 h⁻¹ at a [PO]/[Cr] ratio of 20,000. In contrast, the TOF of the mononuclear catalyst system in Rieger's research dropped from 67 h⁻¹ to 7 h⁻¹ upon dilution from 2000 to 20,000. Although these catalysts were impressive, they were less active and no high molecular-weight copolymer was obtained [38,39]. Liu et al. reported a series of excellent work about the chiral dinuclear cobalt catalysts. By using the chiral dinuclear catalyst, crystalline polycarbonates were obtained [40–42].

It is well known that cocatalysts played very important role in the binary system [43]. Hence, to explore the dinuclear synergy effect with the addition of cocatalyst is a challenging and meaningful work. Intrigued by those successful dinuclear complexes, we designed rigid linked dinuclear catalysts (Fig. 1, complex 2) and evaluated it for PO and CO₂ copolymerization with bis(triphenylphosphine) iminium chloride (PPNCl) as cocatalyst. **Complex 2** was proved to be highly efficient for PO and CO₂ copolymerization. To the best of our knowledge, it provided the highest

* Corresponding author. Fax: +86 431 85262116.
E-mail address: xpang@ciac.ac.cn (X. Pang).

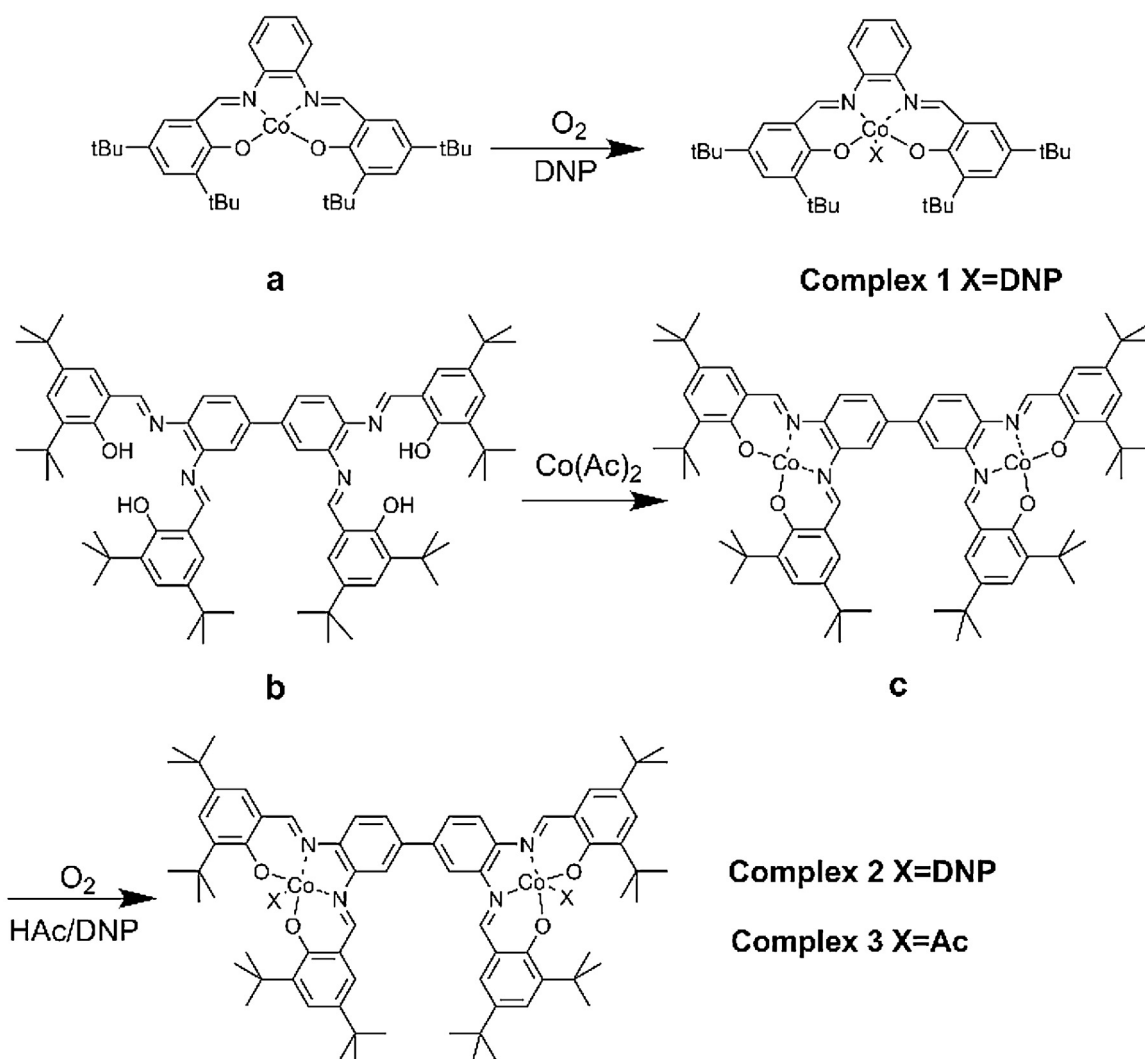


Fig. 1. Synthetic pathway for the preparation of mononuclear and dinuclear catalysts.

molecular weight polycarbonates ($M_n = 200,000$) reported for dinuclear catalysts heretofore. And the two metal center synergy was also observed in presence of cocatalyst. In comparison, we also synthesized a mononuclear salen-Co(III) catalyst (Fig. 1, **complex 1**) which is one half of the dinuclear salen-Co(III) catalyst structurally.

2. Experimental

2.1. Materials and characterization

All manipulations were carried out using standard Schlenk techniques under a dry argon atmosphere or an argon-filled glovebox. Propylene oxide and cyclohexene oxide were distilled from CaH_2 under argon atmosphere. CO_2 (99.95%) was purchased from Siping Jianxin Gas Company and used as received. Solvents were purchased from Aldrich and used as received.

NMR spectra were recorded on Bruker AV 400 M in CDCl_3 at 25°C . Chemical shifts were given in parts per million from tetramethylsilane. Gel permeation chromatography (GPC) measurements were conducted with a Waters 515 GPC with CHCl_3 as eluent. The molecular weights were calibrated against Polystyrene (PS) standards. Differential scanning calorimetry (DSC) was carried out with a TA Q100 thermal analyzer.

2.2. Copolymerization

All copolymerization were performed in 25 mL steel autoclaves. The autoclaves were heated to 110°C for 12 h, then cooled down to room temperature in glovebox prior to use.

Catalysts, cocatalyst and PO/CHO in desired ratio were added into an autoclave. The autoclave was sealed, filled with CO_2 and heated to the desired temperature. When the reaction reached completion, CO_2 was released slowly. Then a sample of crude reaction mixture was taken for ^1H NMR test. The remainder was dissolved with CH_2Cl_2 and slowly dropped into acidified (HCl) methanol. The PPC/PCHC precipitated immediately, and then the process was repeated three times. The copolymer was dried under vacuum at 50°C before analysis by GPC in CHCl_3 .

The diblock copolymer of PPC-PCHC was synthesized by one-pot method. PO, catalyst, cocatalyst and CO_2 were added into the autoclave. After a period of time, when PO reached completion, CHO was added. Intermediate product was taken for ^1H NMR test. When the reaction reached completion, CO_2 was released slowly. The processing procedure of diblock copolymer was the same as for the PPC/PCHC. The sequence could be changed by adding CHO first. The random copolymer of PPC-PCHC was synthesized as the recipe of PPC by adding PO and CHO in desired ratio.

2.3. Preparations of catalysts

Complex a: **complex a** was synthesized as reported method [44,45].

Complex 1: 2,4-Dinitrophenolato (0.19 g, 1.01 mmol) and LiCl·H₂O (0.15 g, 1.68 mmol) were added to the stirred solution of **complex a** (1.00 g, 0.84 mmol) in CH₂Cl₂ (100 mL). The solution was stirred under dry oxygen atmosphere at room temperature for 8 h. The solution was extracted with saturated solution of NaHCO₃ (20 mL × 3), the combined organic layers were dried by MgSO₄. Solvent was removed by vacuum to obtain a dark red solid for further use. The yield is 80%.

Complex b: **complex b** was synthesized as reported method [46].

Complex c: **complex c** was prepared as followed, a mixture of **complex b** (1.00 g, 0.93 mmol) and cobalt acetate (0.33 g, 1.86 mmol) was added in methanol (100 mL) under an atmosphere of argon. The reaction mixture was stirred for 2 h, turning brick-red in several minutes. The product was collected by filtration and rinsed with cold methanol (3 × 10 mL), then dried under vacuum at 50 °C. The yield is 95%.

Complex 2: 2,4-Dinitrophenolato (0.40 g, 2.17 mmol) and LiCl·H₂O (0.15 g, 2.52 mmol) were added to the stirred solution of **complex c** (1.00 g, 0.84 mmol) in CH₂Cl₂ (100 mL). The solution was stirred under oxygen atmosphere at room temperature for 8 h. The solution was extracted with saturated solution of NaHCO₃ (20 mL × 3), the combined organic layers were dried by MgSO₄. The solvent was removed by vacuum to obtain a dark red solid for further use. The yield is 80%. (please see Supporting information for ¹H NMR and MS results of **complex 2**).

Complex 3 was synthesized with the same procedure used for **complex 2**, using acetic acid instead of 2,4-dinitrophenolato. **Complex 3** was investigated for copolymerization, and it was inferior to **complex 2** in PO and CO₂ copolymerization (Table S3 in Supporting information).

3. Results and discussion

3.1. Comparison of complex 1 with complex 2 in various conditions

Mononuclear **complex 1** and dinuclear **complex 2** were investigated for PO and CO₂ copolymerization (Table 1). The rigid dinuclear structure was conjugated, as the ¹H NMR spectrum showed in Fig. S5 in Supporting information [44,45]. It was suggested that an electron transfer bridge existed between the two cobalt atoms in **complex 2**, which could increase the activity and stability during copolymerization. The dinuclear catalyst was more active than the mononuclear catalyst in certain conditions such as high dilution and high temperature. The selectivity and activity for **complexes 1** and **2** were sensitive to reaction temperature (Figs. 2 and 3). When the reaction temperature was higher than 60 °C, back-biting reactions were severe, the fraction of cyclic(propylene carbonate) (cPC) increased for **complex 1** (Fig. 2). At 60 °C, the mononuclear catalyst system (**complex 1** and PPNCI) obtained more cPC (18%), while the dinuclear catalyst system (**complex 2** and PPNCI) still maintained its stability with only 2% cPC (Fig. 2). The dinuclear catalyst system showed conversion of PO as high as 65% at 90 °C, and the mononuclear catalyst system showed only 12% (Fig. 3).

Complex 2 also showed great merit in high dilutions. For example, at [PO]/[Cat] = 20,000, **complex 1** almost lost its activity (TOF = 3 h⁻¹) and no detectable polymers were observed, while **complex 2** showed TOF of 406 h⁻¹, 135 times higher than that of **complex 1** (Table 1, Entries 8 and 14). **Complex 2** provided copoly-

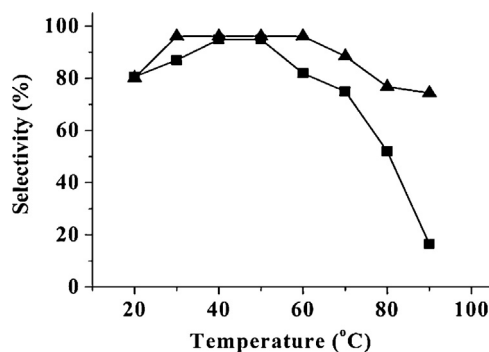


Fig. 2. The effect of the temperature on selectivity using **complex 1** (■) and **complex 2** (▲), [PO]/[Cat]/[cocat] ratio was 5000:1:1.

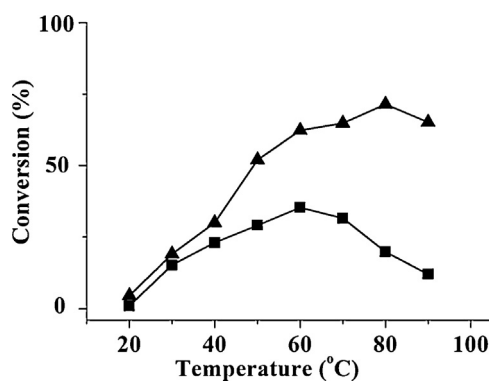


Fig. 3. The effect of the temperature on activity using **complex 1** (■) and **complex 2** (▲), [PO]/[Cat]/[cocat] ratio was 5000:1:1, 2 MPa, 2 h.

mer with molecular weight as high as 200,000, while only 57,000 for **complex 1** (Table 1, Entries 7 and 13). It was notable that the highest reported molecular weight was 46,000 by other dinuclear catalysts [38]. In high dilution, **complex 2** maintained selectivity as high as 93%, while only 15% for **complex 1** (Table 1, Entries 8 and 14). **Complex 2** still maintained its high selectivity (98% chain copolymer), while only 75% for **complex 1** at high PO conversion (Table S1 in Supporting information, Entries 7 and 14).

3.2. Kinetic studies of the PO/CO₂ copolymerization

In order to gain an insight into the propagation mechanism, further research focused on the chain propagation process. Liu et al. reported that the addition of cocatalyst would cause the induction period as a negative intermolecular effect, and the loading of cocatalyst determined the length of the induction period [47]. In our work, **complexes 1** and **2** showed different induction period as shown in Fig. 4a and b. **Complex 1** showed a typical induction period (Fig. 4a), the selectivity of PPC dropped to as low as 23% at 5 min with 1 eq cocatalyst. When employed in high dilution, the induction period was prolonged to more than 2 h (Table S1 in Supporting information, Entries 15 and 17). By contrast, **complex 2** showed a shorter induction period and weaker inductive influence (82% PPC at 5 min with 1 eq cocatalyst, Fig. 4b). We temporally suggested that the difference was mainly due to the intramolecularly cooperative effect in **complex 2**, which could suppress the impact introduced by the addition of cocatalyst.

The loading of cocatalyst was of importance during the copolymerization process. It was notable that the dinuclear catalyst showed constant selectivity (>99% PPC, 5 min) with 0.5 eq cocatalyst in the induction period (Table S2 in Supporting information, Entry 1). And if the dinuclear catalyst was employed with 2 eq cocatalyst, the selectivity of PPC was poor in the induction period

Table 1Copolymerization of CO₂ and PO by **complex 1** and **2** in different [PO]/[Cat] ratios.^a

Entry	Cat.	[PO]/[Cat] ^b	[Cocat]/[Cat] ^b	Time (h)	Con (%) ^c	TOF (h ⁻¹) ^d	PPC (%) ^e	Mn (kg mol ⁻¹) ^f	PDI ^f
1	2	1000	N/A	0.5	0.15	1.5	>99	N/A	N/A
2	2	2000	0.5	1	25	254	>99	19	1.21
3	2	2500	1	1	74	925	98	38	1.28
4	2	5000	1	2	73	908	98	58	1.21
5	2	7500	1	2	39	738	98	89	1.15
6	2	10000	1	4	56	695	96	106	1.17
7	2	10000	1	13	82	314	81	200	1.31
8	2	20000	1	8	32	406	93	52	1.20
9	2	40000	1	24	5	45	21	8	1.05
10	1	2500	1	2	54	674	86	18	1.46
11	1	5000	1	2	35	884	82	23	1.20
12	1	7500	1	2	23	855	90	47	1.17
13	1	10000	1	8	38	477	80	57	1.20
14	1	20000	1	24	0.36	3	15	N/A	N/A

^a The reactions were performed in 2 mL neat PO and 25 mL autoclave at 60 °C, 2 MPa. Without extra illustration, the selectivity of carbonate units over polyether units was >99%.

^b Molar ratio.

^c The results based on the amount of converted PO by ¹H NMR spectroscopy.

^d Turnover frequency (TOF) = mol of product/mol of cobalt center per hour.

^e Selectivity for polycarbonates over cyclic carbonate, determined by ¹H NMR spectroscopy.

^f Determined by gel permeation chromatography, calibrated with polystyrene.

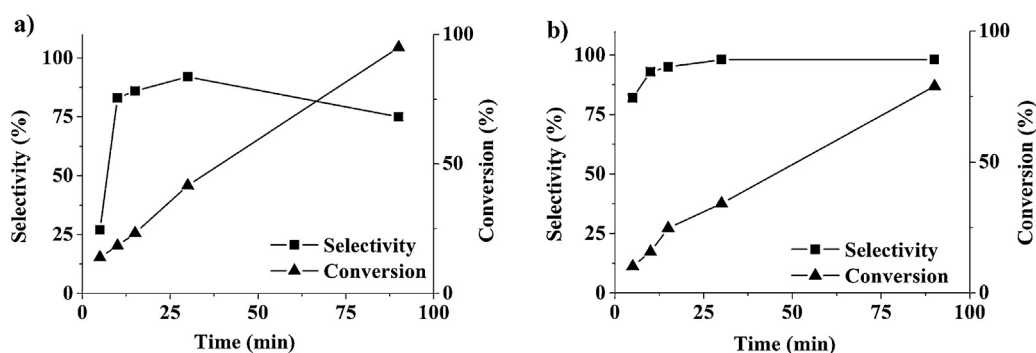


Fig. 4. The induction period using **complex 1** and **2**. a: **complex 1**, [PO]/[Cat]/[cocat] ratio was 1000:1:1; b: **complex 2**, [PO]/[Cat]/[cocat] ratio was 2500:1:1.

as the mononuclear catalyst showed (Table S1 in Supporting information, Entry 8). At the same time, reduction of the loading of cocatalyst for **complex 1** did not eliminate the induction period (Table S1 in Supporting information, Entry 9). Different byproducts were obtained by the dinuclear catalyst under low CO₂ pressure, and the amount of cocatalyst could determine the product composition. At [cocat]/[Cat] ratio of 1:1, 0.2 MPa of CO₂, the dinuclear catalyst system obtained 20% polyether and only 6% cPC as byproduct. Under the same conditions, the mononuclear catalyst system obtained nearly no polyether units in the polymer chain and 25% cPC. As the loading of cocatalyst increased, **complex 2** produced few polyether and only cPC as byproduct (Table S2 in Supporting information, Entries 7–9).

3.3. Proposed mechanism for the dinuclear catalyst

Based on the above research, it was believed that the number of cocatalyst was important in the chain propagation process, and we temporally proposed a mechanism for the dinuclear catalyst system (Fig. 5). As shown in Fig. 5, PO was activated on metal centers to form intermediate **I**, and the nucleophile Cl⁻ attacked the activated PO on random side. Not all the activated PO could be attacked by Cl⁻ since the amount of Cl⁻ from cocatalyst was not enough. Then, CO₂ inserted into the metal alkoxide bond (intermediate **II**), forming the carbonate unit (intermediate **III**). The growing copolymer chain could migrate to the other metal center and attack the activated PO (intermediate **IV**), which was supposed as the key process for the bimetallic synergism. The chain migra-

tion would be fast, as all polymers obtained owned low PDIs. As proposed, the PO insert step was accelerated by this process. The copolymer chain could immediately propagate with the activated PO on the other metal center after the CO₂ insert step (intermediate **V**). With PO and CO₂ inserted into the carbonate chain (**VI**), target copolymer PPC was obtained. The polyether was obtained when the CO₂ insert step was slowed down in low CO₂ pressure. By contrast, few polyether units were obtained under the same CO₂ pressure when employed the mononuclear catalyst. This process would also enhance the selectivity of chain copolymer as discussed in supporting information (Fig. S8). Similar bimetallic mechanism was suggested by Nozaki and other researchers [36,38,39,41,48,49]. With enough cocatalyst, the dinuclear catalyst would catalyze the PO and CO₂ copolymerization as the way mononuclear catalyst did via the mononuclear mechanism (Fig. 6) [29,38,39]. With different loading of cocatalyst, the dinuclear catalyst could adopt in three different states: A) with no cocatalyst involved, catalysts almost lost its activity; B) with 1 eq cocatalyst involved, catalysts acted via the proposed mechanism: more active and selective (as shown in Figs. 2 and 3); C) with 2 eq cocatalyst involved, catalysts acted via the mononuclear mechanism, and showed lower activity and selectivity. The real states would be a combination of at least two of the three states, which were determined by the loading of cocatalyst.

Further investigation supported our mechanism: the activity and selectivity of the dinuclear catalyst changed with the change of cocatalyst loading (Fig. 7). When the copolymerization proceeded at [cocat]/[Cat] ratio of 0.5:1, the majority of catalysts was in states **A** and **B**, the selectivity was high but the activity was low. When

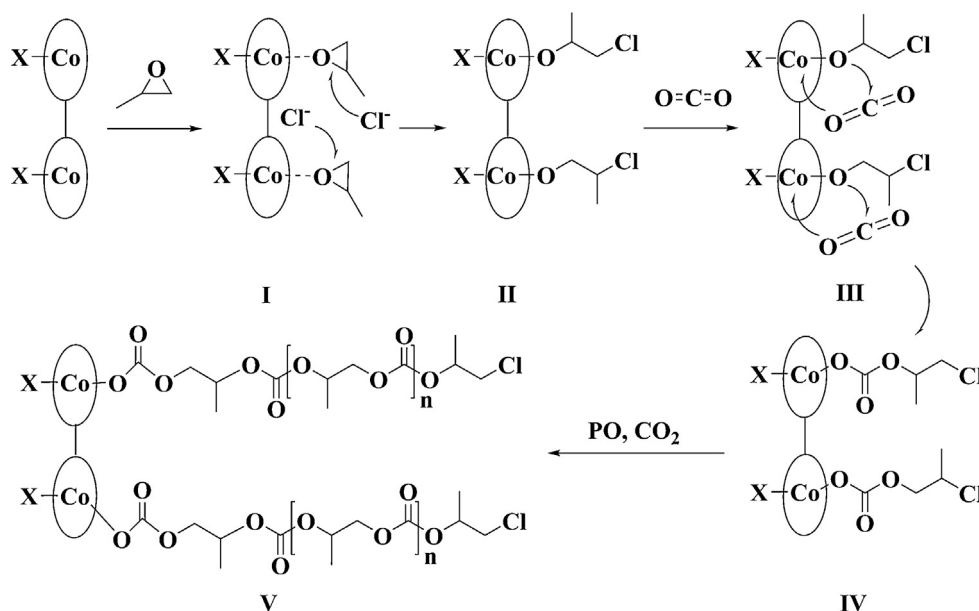


Fig. 5. Proposed bimetallic mechanism for the CO₂ and PO copolymerization.

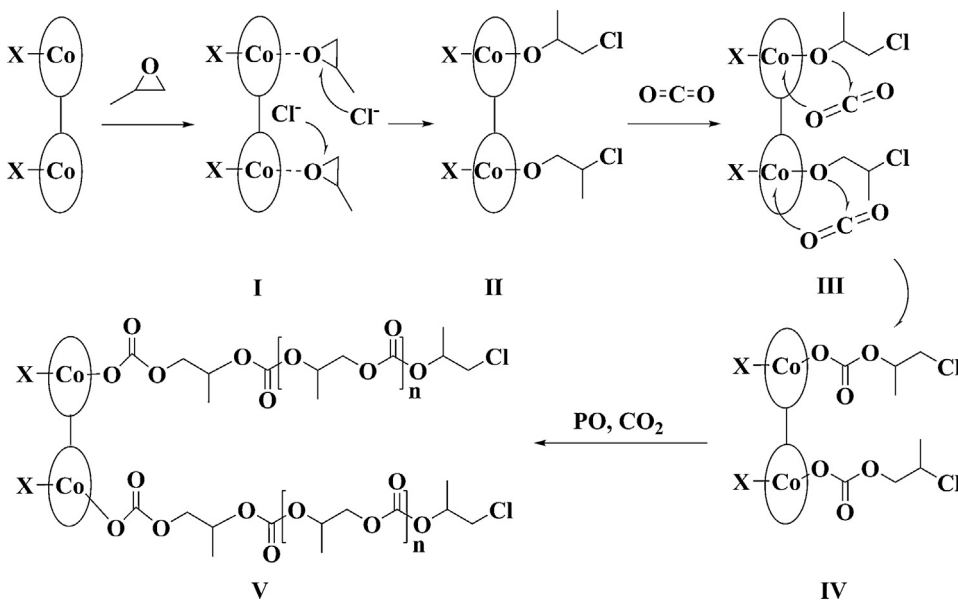


Fig. 6. Propagation process by the mononuclear mechanism.

the copolymerization proceeded at [cocat]/[Cat] ratio of 1:1, the catalyst in state **A** became less and the catalyst in state **B** increased, hence, the activity increased; due to the existence of state **C**, the selectivity decreased slightly. When the [cocat]/[Cat] ratio was at 1.2–1.5:1, catalyst in state **A** reduced further, so the activity continued to increase; there would be more catalyst in state **C**, the selectivity decreased further. When the [cocat]/[Cat] ratio was at 2:1, most of catalyst was in state **C**, which showed the lowest selectivity. The decrease in activity at the same time proved that the catalyst in state **C** proceeded the chain propagation slowly than in state **B**.

3.4. The diblock and random copolymer of PPC-PCHC

Although the high molecular-weight PPC was obtained in this work, there still have spaces to be improved for the glass transformation temperature (T_g) to meet the request in some applications.

As the thermal and mechanical properties of polymer could be modified by incorporating with other polymers [24], we tried to enhance the T_g of PPC by this method. Cyclohexene oxide (CHO) was an attractive epoxide for copolymerization with CO₂, the poly(cyclohexene carbonate) (PCHC) showed higher T_g than that of PPC. As mentioned in Section 3.1, when PO reached completion, the reaction system with **complex 2** was stable and no depolymerization occurred. Meanwhile, this reaction was somewhat “immortal”. With the addition of CHO monomer, the copolymerization would continue. The diblock copolymer of PPC-PCHC with narrow polydispersities (PDI) was obtained by this method. The mixture of PPC and PCHC showed two T_g s, while the diblock copolymer only showed one T_g (Fig. 8), indicating the complete formation of diblock copolymers. As predicted, the T_g of the diblock copolymer was higher than PPC. The proportion of PPC and PCHC units in the diblock copolymers could be calculated by ¹H NMR. The T_g value enhanced little when the proportion of PCHC was less than 30%. Due to the low

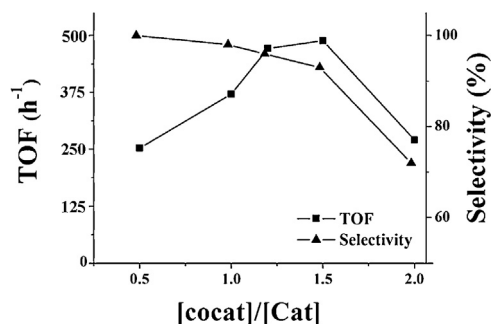


Fig. 7. The effect of the cocatalyst loading on activity and selectivity using complex 2. [PO]/[Cat] ratio was 2000:1.

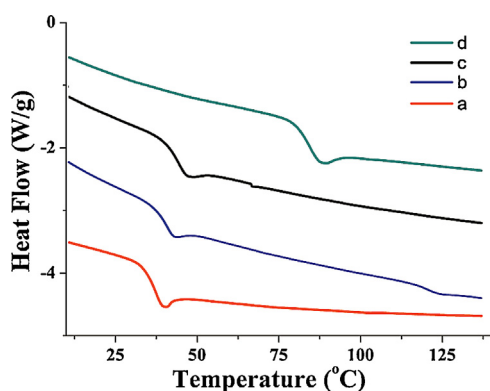


Fig. 8. The DSC curves: a) PPC; b) the mixture of PPC and PCHC; c) the diblock copolymer of PPC-PCHC; d) the random copolymer of PPC-PCHC.

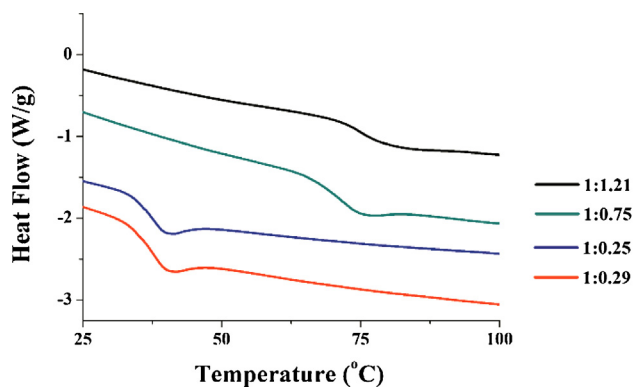


Fig. 9. The DSC curves of random copolymers with different [PPC]:[PCHC] ratios.

activity of CHO in this reaction, it was hard to control the composition of the diblock copolymer.

Then, the random copolymers of PPC-PCHC were prepared to further enhance the T_g . The T_g value of the random copolymer of PPC-PCHC is shown in Fig. 8. The random copolymer of PPC-PCHC showed only one T_g with narrow PDI. Similar conclusion was obtained in previous work by Shi et al. [50]. The T_g s of the random copolymers of PPC-PCHC were enhanced remarkably and it could be easily adjusted by changing the feed ratio of [PO]/[CHO]. A series of PPC/PCHC random copolymers with different compositions were obtained. The T_g s were related with the incorporation of PCHC units as predicted, but the relationship did not fit the Flory–Fox empirical equation [40]. As the ratio of [PPC]/[PCHC] was near 1:1, the T_g s of random copolymers were obviously enhanced (Fig. 9). More PCHC units in the random copolymer caused a decreased in T_g (Table S5 in Supporting information, Entry 5). Notably, the T_g s of random

copolymers also depended on reaction conditions (See Table S5 in Supporting information for detailed preparation of random copolymers). We regarded the arrangement of the PPC and PCHC units was important for the change of T_g s. Approximately equal TOFs of PO and CHO in copolymerization led to PPC-PCHC random copolymer with higher T_g values, Lu assumed that the alternating nature of the two different carbonate units was predominant, and the alternating structure of PPC and PCHC units was the major sequence [50]. Lu et al. also reported the PPC-PCHC copolymer with a [PPC]:[PCHC] ratio of 1:0.67, which showed T_g as high as 68.8 °C [50]. While PPC-PCHC random copolymer with a [PPC]:[PCHC] ratio of 1:1.1 in this work showed T_g as high as 86.78 °C (Table S5 in Supporting information, Entry 9).

4. Conclusions

In summary, we have compared the mononuclear and dinuclear catalysts system in PO and CO₂ copolymerization. The dinuclear catalyst system was highly active and selective, PPC with high molecular-weight was obtained. A mechanism based on the conjugated dinuclear structure was proposed. The induction period and low CO₂ pressure effect was typical features of proposed mechanism. The diblock and random copolymer of PPC-PCHC was synthesized to obtain better thermal property. The glass transformation temperature of the random copolymer of PPC-PCHC was obviously enhanced and was easily to adjust. Further studies aimed at understanding the detailed mechanisms of dinuclear system and thermal properties of copolymers are underway.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2015.10.019>.

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